

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-012730

(43)Date of publication of application : 19.01.1999

(51)Int.Cl.

C23C 14/34

C23C 14/14

(21)Application number : 09-164690

(71)Applicant : NEC CORP

(22)Date of filing : 20.06.1997

(72)Inventor : TSUBOI SHINJI

## (54) PRODUCTION OF THIN CHROMIUM FILM

## (57)Abstract:

PROBLEM TO BE SOLVED: To form a thin Cr film of low stress, excellent in adhesion to a substrate, by using an He-Ar gaseous mixture of specific composition as a sputter gas in case of forming a Cr film on a substrate by a sputtering method by the use of Cr as a sputtering target.

SOLUTION: At the time of forming a thin Cr film of integrated circuit pattern, etc., on a conductive substrate, such as silicon wafer, or an insulating substrate of glass, synthetic resin, etc., by a sputtering method by the use of Cr as a sputtering target, an He-Ar gaseous mixture consisting of 5 to 25 vol.% Ar gas and the balance He gas is used as a sputter gas. When the mixing ratio of Ar gas is less than 5%, plasma is not stabilized and sputtering becomes difficult; when it exceeds 25%, the amount of supply of He incorporated is decreased and stress controlling property becomes deteriorated. By this method, pressure control can be facilitated, and the thin Cr film can be formed in high yield.

## LEGAL STATUS

[Date of request for examination] 20.06.1997

[Date of sending the examiner's decision of rejection] 09.10.2002

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

5 - 25% Ar  
75 - 95% He

[Patent number]

[Date of registration]

[Number of appeal against examiner's  
decision of rejection]

[Date of requesting appeal against examiner's  
decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2000 Japan Patent Office

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## DETAILED DESCRIPTION

### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention is concerned with the process which forms a detailed integrated-circuit pattern on a semiconductor wafer, and relates to the manufacture method of the chromium thin film by the spatter which can control membraneous quality with repeatability detailed and sufficient at low temperature.

[0002]

[Description of the Prior Art] The chromium thin film obtained by the spatter is excellent in adhesion with glass, thermal resistance, and opposite chemical nature, and is widely used as shading material of the wiring material of a liquid crystal display, or a photo mask. although the thing of low stress [ thin film / chromium / which is used for these ] is recently called for with detailed-izing of a device -- a Prior art -- enough -- low -- the stress chromium thin film was not obtained

[0003]

[Problem(s) to be Solved by the Invention] The trouble of the conventional technology is as follows.

[0004] Although the spatter which mainly uses Ar as spatter gas had been used when forming a chromium thin film on the ground of a substrate and others, when chromium was formed by this spatter, there was a fault which very big stress produces. When this trouble has big stress, and the wafer of a substrate curves, for example, I hear that position \*\*\*\*\* of a pattern will shift and the product yield will fall, and there is.

[0005] By the way, in case Cr is formed by the spatter on an insulating substrate, the manufacture method of Cr thin film using the argon gas which contained nitrogen 0.1 to 10% as spatter gas is indicated by JP,3-36259,A. It is indicated that Cr thin films obtained by this method are low stress and low resistance.

[0006] However, since the 1st trouble of this technology makes spatter gas what mixed nitrogen into argon gas, the thin film actually formed is in being not a chromium thin film but the nitriding chromium thin film CrNx. The reason is in nitriding chromium dissolving by the above-mentioned method.

[0007] Compared with a chromium thin film, I hear that a nitriding chromium thin film has weak adhesion with a ground, and the 2nd trouble has it. Although stress does not produce peeling by own stress of a film etc. for a low reason, a nitriding chromium thin film will become easy to peel from a ground, if external force, such as vibration, is added.

[0008] The 3rd trouble is \*\*\*\*\*ing by ashing processing according [ a nitriding chromium thin film ] to oxygen plasma. In the process which produces a photo mask, since it surely passes through the step of the ashing processing by oxygen plasma, a nitriding chromium thin film can be used.

[0009] The purpose of this invention method solves these troubles, and is to offer the manufacture method of the chromium thin film which fully made stress low stress.

[0010]

[Means for Solving the Problem] As a result of inquiring wholeheartedly to solve the above-mentioned technical problem, in manufacture of the chromium thin film to a ground top, by forming as spatter gas

what mixed 5 - 25% of argon gas in helium gas by setting a spatter target to Cr, this invention person finds out that the chromium thin film of low stress with sufficient adhesion with a ground can be formed, and came to complete this invention.

[0011] That is, this invention is the manufacture method of the chromium thin film characterized by using the helium which mixed the argon of 5 or 25 capacity % as spatter gas in the manufacture method of the chromium thin film which uses Cr for a spatter target and forms chromium by the spatter on a ground.

[0012] Although the stress control by the pressure of spatter gas was difficult in order to change from compressive stress to a tensile stress rapidly in a low stress field, if it carries out using only an argon as spatter gas when using Cr for a spatter target and forming chromium by the spatter In this invention, in case Cr is formed in the usual sputtering system, by using the helium which mixed the argon gas of 5 - 25 capacity % as spatter gas (using gaseous helium capacity as the base) A chromium thin film is formed and the controllability of stress improves by the bird clapper that the inclination of the slope which changes with spatter gas \*\* from compressive stress to a tensile stress is loose. This is for the helium of spatter ion being incorporated by the chromium thin film, and shifting to compressive stress by using helium with the atomic number smaller than an argon for spatter gas.

[0013] If there are few mixing rates of an argon than 5 capacity %, since plasma is stabilized and is not formed, it will become difficult to carry out a spatter. The amount of supply of the helium which will be incorporated on the other hand if 25 capacity % is exceeded decreases, and stress-control nature serves as as with it being bad like the case where a spatter is carried out only with an argon.

[0014]

[Embodiments of the Invention] The manufacture method of the chromium thin film of this invention can carry out and carry out things to a spatter target in the arbitrary usual sputtering systems known conventionally uses Cr.

[0015] Formation of the chromium thin film used as a gestalt of suitable operation of this invention method in the process which forms a detailed integrated-circuit pattern on the production technology of a semiconductor integrated circuit, i.e., a semiconductor wafer, for example is applicable.

[0016] As for the ground which forms a chromium thin film on it, the grounds in which a substrate and others are arbitrary may be applicable. As a substrate, both of insulating substrates, such as conductive substrates, such as a silicon wafer, glass, and synthetic resin, are applicable.

[0017]

[Example] Hereafter, although an example shows this invention concretely, this invention is not limited to this and can be suitably changed within the limits of this invention.

[0018] The 4 inches raise in basic wages silicon substrate (480-micrometer \*\*) was installed in RF sputtering system (the product made from Anelva, SPF-530H), and sputtering was performed by 4-N 6 inches and Cr target of 3mm \*\*, and spatter power 800W. At this time, as spatter gas, helium was introduced into 50sccm(s), the argon was introduced in equipment by the flow rate of 5sccm(s), sputtering was performed, without performing substrate heating, and the chromium thin film of 50nm of thickness was formed. When various gas \*\* were changed and membranes were formed, as shown in drawing 1, the chromium thin film changed from compressive stress to the tensile stress by 4 - 6mTorr, and it became about 0 stress by 5mTorr.

[0019] In addition, although gaseous helium and argon gas were mixed within equipment by the above-mentioned method, even if it uses for gaseous helium the gas which mixed argon gas from the first, it cannot be overemphasized that the same effect is acquired.

[0020] The result which only the argon was introduced in equipment by the flow rate of 55sccm(s) as spatter gas, and also sputtering was performed on the same conditions as the case of the above-mentioned example, and various gas \*\* were changed, and formed chromium of 50nm of thickness for comparison is shown in drawing 2. The pressure field where stress becomes 0 is narrow so that drawing 2 may see, and stress control is difficult.

[0021] In the case of the example of this invention, the pressure field where stress becomes 0 compared with the case where only an argon is used as spatter gas is large, and it is possible to form a stress free-

$5\text{ sccm} = \frac{\text{cm}^3}{\text{min}}$

deposition rate

lancer's chromium thin film easily so that clearly [ result / which is shown in drawing 1 ] as compared with this.

[0022]

[Effect of the Invention] According to this invention, although the pressure control for controlling stress was difficult in the conventional method which forms Cr film, using only an argon as spatter gas as explained above, since it is obtained even if the chromium thin film of low stress carries out stress change to some extent, pressure control becomes easy and a chromium thin film can be formed with the sufficient yield.

[0023] Moreover, although the low stress chromium thin film (in fact nitriding chromium thin film) which used nitrogen had a problem in adhesion with a ground, the chromium thin film of this invention is excellent also in adhesion.

[0024] Furthermore, since the ashing processing by the oxygen plasma currently generally used will \*\*\*\*\* when a nitriding chromium thin film exfoliates a resist, the process which can be used will be restricted. On the other hand, even if the low stress chromium thin film formed by the method of this invention performs ashing processing, it does not \*\*\*\*\*.

---

[Translation done.]

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

CLAIMS

---

[Claim(s)]

[Claim 1] The manufacture method of the chromium thin film characterized by using the helium which mixed the argon of 5 or 25 capacity % as spatter gas in the manufacture method of the chromium thin film which uses Cr for a spatter target and forms chromium by the spatter on a ground.

[Claim 2] The manufacture method of a chromium thin film according to claim 1 that the aforementioned ground is a conductive substrate.

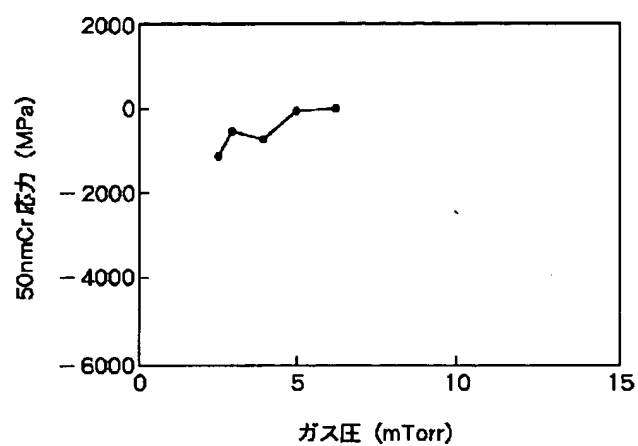
[Claim 3] The manufacture method of a chromium thin film according to claim 1 that the aforementioned ground is an insulating substrate.

---

[Translation done.]

Drawing selection ☐ [Representative drawing] ☒

---



[Translation done.]

MENU

SEARCH

INDEX

1/1



JAPANESE PATENT OFFICE

## PATENT ABSTRACTS OF JAPAN

(11)Publication number: 11012730

(43)Date of publication of application: 19.01.1999

1-19-99

(51)Int.Cl.

C23C 14/34  
C23C 14/14

(21)Application number: 09164690

(71)Applicant:

NEC CORP

(22)Date of filing: 20.06.1997

(72)Inventor:

TSUBOI SHINJI

(54) PRODUCTION OF THIN CHROMIUM FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To form a thin Cr film of low stress, excellent in adhesion to a substrate, by using an He-Ar gaseous mixture of specific composition as a sputter gas in case of forming a Cr film on a substrate by a sputtering method by the use of Cr as a sputtering target.

SOLUTION: At the time of forming a thin Cr film of integrated circuit pattern, etc., on a conductive substrate, such as silicon wafer, or an insulating substrate of glass, synthetic resin, etc., by a sputtering method by the use of Cr as a sputtering target, an He-Ar gaseous mixture consisting of 5 to 25 vol.% Ar gas and the balance He gas is used as a sputter gas. When the mixing ratio of Ar gas is less than 5%, plasma is not stabilized and sputtering becomes difficult; when it exceeds 25%, the amount of supply of He incorporated is decreased and stress controlling property becomes deteriorated. By this method, pressure control can be facilitated, and the thin Cr film can be formed in high yield.

## LEGAL STATUS

[Date of request for examination]

20.06.1997

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

5-25% Ar  
75-95% He

Copyright (C) 1998 Japanese Patent Office

MENU

SEARCH

INDEX



特11-012730

Page 1.

(10) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開 号

特開平11-12730

(43) 公開日 平成11年(1999) 1月19日

(51) IntCl<sup>8</sup>C 23 C 14/34  
14/14

識別記号

P I

C 23 C 14/34  
14/14M  
D

審査請求 有 請求項の数 3 O L (全 3 頁)

(21) 出願番号 特願平8-164690

(22) 出願日 平成9年(1997) 6月20日

(71) 出願人 000004237

日本電気株式会社

東京都港区芝五丁目7番1号

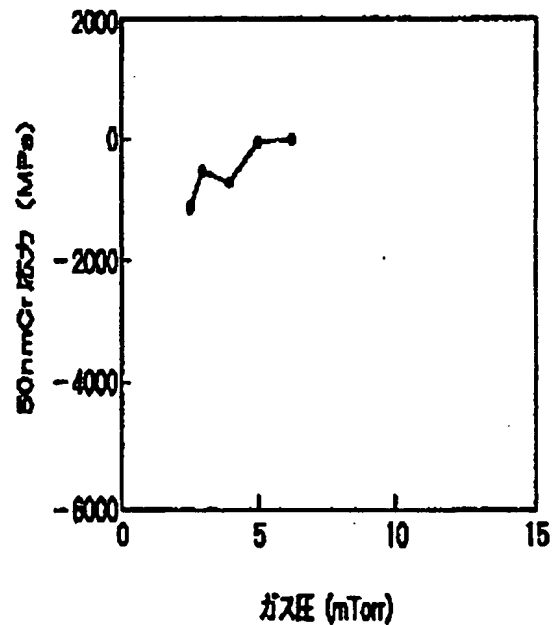
(72) 発明者 野井 伸二

東京都港区芝五丁目7番1号 日本電気株  
式会社内

(74) 代理人 弁護士 若林 忠

(54) 【発明の名称】 クロミウム薄膜の製造方法

(57) 【要約】

【課題】 下地上にスパッタ法によりクロミウム薄膜を  
成膜する際、得られる薄膜の応力を十分に低応力にする  
成膜法を提供する。【解決手段】 スパッタ時のスパッタガスとして5ない  
し25容量%のアルゴンを混合したヘリウムを用いる。

【0015】本発明方法の好適な実施の形態としては、たとえば半導体集積回路の作製技術、すなわち半導体ウエハ上に微細な集積回路パターンを形成するプロセスにおいて用いるクロミウム薄膜の形成が対象となる。

【0016】クロミウム薄膜をその上に形成する下地は、基板その他の任意の下地が対象となりうる。基板としてはシリコンウエハ等の導電性基板、ガラス、合成樹脂等の絶縁基板のどちらも対象となる。

【0017】

【実施例】以下、実施例により本発明を具体的に示すが、本発明はこれに限定されるものではなく、適宜本発明の範囲内で変更できるものである。

【0018】4インチのペアシリコン基板(480mm厚)をRFスパッタ装置(アネルバ製、SPF-530H)内に設置して、4N6インチ、3mm厚のCrターゲット、スパッタパワー800Wでスパッタリングを行った。この時、スパッタガスとしてヘリウムを50sccm、アルゴンを5sccmの流量で装置内に導入し、基板加熱を行わずにスパッタリングを行い、膜厚50nmのクロミウム薄膜を形成した。ガス圧を種々変化させて成膜したところ、図1に示すように4~6mTorrでクロミウム薄膜が圧縮応力から引張り応力に変化し、5mTorrでほぼ0応力となった。

【0019】なお、上記の方法では、ヘリウムガスとアルゴンガスを装置内で混合したが、元々、ヘリウムガスにアルゴンガスを混合したガスを用いても同様の効果が得られることはいうまでもない。

【0020】比較のために、スパッタガスとしてアルゴンのみを55sccmの流量で装置内に導入した他は、上記実施例の場合と同一条件でスパッタリングを行い、ガス圧を種々変化させて膜厚50nmのクロミウムを成

膜した結果を図2に示す。図2にみられるように応力が0となる圧力領域が狭く、応力制御が困難である。

【0021】図1に示す結果をこれと比較すると明らかに、本発明の実施例の場合はアルゴンのみをスパッタガスとして使用した場合に比べ応力が0となる圧力領域が広く、容易にストレスフリーのクロミウム薄膜を形成することが可能である。

【0022】

【発明の効果】以上説明したようにアルゴンのみをスパッタガスとして用いてCr膜を形成する従来法では、応力を制御するための圧力制御が困難であったが、本発明によれば、低応力のクロミウム薄膜がある程度応力変動しても得られることから、圧力制御が容易となり、歩留りよくクロミウム薄膜が成膜できる。

【0023】また、窒素を用いた低応力クロミウム薄膜(実際には窒化クロミウム薄膜)は下地との密着性に問題があったが、本発明のクロミウム薄膜は密着性にも優れている。

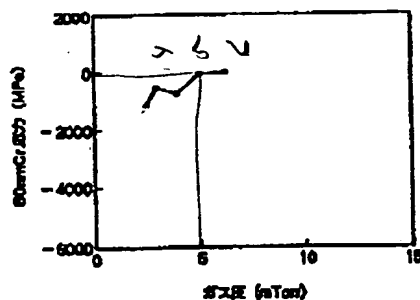
【0024】さらに、窒化クロミウム薄膜はレジストを剥離するとき一般的に使用されている融薬プラズマによる灰化処理により、エッチングされてしまうため、使用できるプロセスが限られてしまう。一方、本発明の方法で形成された低応力クロミウム薄膜は灰化処理を行ってもエッチングされることはない。

【図面の簡単な説明】

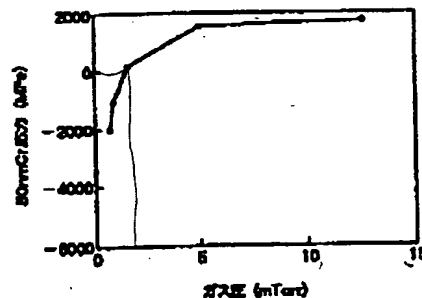
【図1】本発明の実施例の方法でスパッタした場合のスパッタ時ガス圧と得られたクロミウム薄膜の応力の関係を示すグラフ

【図2】従来のアルゴンをスパッタガスとする方法でスパッタした場合のスパッタ時ガス圧と得られたクロミウム薄膜の応力の関係を示すグラフ

【図1】



【図2】



## 【特許請求の範囲】

【請求項1】 スパッタターゲットにCrを用い下地上にスパッタ法によりクロミウムを成膜するクロミウム薄膜の製造方法に於いて、スパッタガスとして5ないし25容量%のアルゴンを混合したヘリウムを用いることを特徴とするクロミウム薄膜の製造方法。

【請求項2】 前記下地が導電性基板である、請求項1に記載のクロミウム薄膜の製造方法。

【請求項3】 前記下地が絶縁基板である、請求項1に記載のクロミウム薄膜の製造方法。

## 【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、半導体ウエハ上に微細な集積回路パターンを形成するプロセスにかかわり、詳しくは低温で再現性よく膜質をコントロールできるスパッタ法によるクロミウム薄膜の製造方法に関する。

【0002】

【従来の技術】スパッタ法で得られたクロミウム薄膜は、ガラスとの密着性、耐熱性、耐薬品性に優れており、液晶ディスプレイの配線材料やフォトマスクの透光材として広く利用されている。最近ではデバイスの微細化に伴い、これらに用いられるクロミウム薄膜も低応力のものが求められているが、従来の技術では十分低応力なクロミウム薄膜は得られなかった。

【0003】

【発明が解決しようとする課題】従来の技術の問題点は次のとおりである。

【0004】基板その他の下地上にクロミウム薄膜を形成する際には主にスパッタガスとしてArを用いるスパッタ法が用いられてきたが、クロミウムをこのスパッタ法で成膜すると非常に大きな応力が生じてしまう欠点があった。この問題点は、大きな応力があると、たとえば基板のウエハが反ってしまうことによって、パターンの位置あわせがずれてしまい、製品歩留りが低下してしまうということである。

【0005】ところで、特開平3-36259号公報には、絶縁基板上にスパッタ法でCrを成膜する際に、0.1~10%窒素を含有したアルゴンガスをスパッタガスとして用いるCr薄膜の製造方法が開示されている。この方法で得られるCr薄膜は低応力かつ低抵抗であることが開示されている。

【0006】しかしながら、この技術の第1の問題点はアルゴンガス中に窒素を混入したものをスパッタガスとしているため、実際に成膜される薄膜はクロミウム薄膜ではなく、窒化クロム薄膜CrNxであることにある。その理由は上記の方法では窒化クロムが固着してしまうことにある。

【0007】第2の問題点は窒化クロム薄膜はクロミウム薄膜に比べ、下地との密着性が弱いということであ

る。窒化クロム薄膜は応力が低いため膜自身の応力によるはがれ等は生じないが、振動などの外力が加わると下地からはがれやすくなる。

【0008】第3の問題点は窒化クロム薄膜は酸素プラズマによる灰化処理でエッチングされてしまうことである。フォトマスクを作製するプロセスでは、酸素プラズマによる灰化処理のステップを必ず経るので、窒化クロム薄膜は使用できないことになる。

【0009】本発明方法の目的は、これらの問題点を解決し、応力を十分に低応力にしたクロミウム薄膜の製造方法を提供することにある。

【0010】

【課題を解決するための手段】本発明者は、上記課題を解決するべく鋭意検討した結果、下地上へのクロミウム薄膜の製造において、スパッタターゲットをCrとしてHeガスに5~25%のアルゴンガスを混合したものをスパッタガスとして成膜することにより、下地との密着性の良い低応力のクロミウム薄膜が形成できることを見出し本発明を完成するに至った。

【0011】すなわち本発明はスパッタターゲットにCrを用い下地上にスパッタ法によりクロミウムを成膜するクロミウム薄膜の製造方法に於いて、スパッタガスとして5ないし25容量%のアルゴンを混合したヘリウムを用いることを特徴とするクロミウム薄膜の製造方法である。

【0012】スパッタターゲットにCrを用いてスパッタ法によりクロミウムを成膜する場合、スパッタガスとしてアルゴンのみを用いて実施すると低応力領域で圧縮応力から引張り応力に急激に変化するためにスパッタガスの圧力による応力制御が困難であったが、本発明では、通常のスパッタ装置にてCrを成膜する際、スパッタガスとして（ヘリウムガス容量をベースにして）5~25容量%のアルゴンガスを混合したヘリウムを用いることにより、クロミウム薄膜が形成され、スパッタガス圧により圧縮応力から引張り応力に変化するスロープの傾きが緩やかとなることで、応力の制御性が向上する。これは、スパッタガスにアルゴンよりも原子番号の小さなヘリウムを用いることによりスパッタイオンのヘリウムがクロミウム薄膜に取り込まれて圧縮応力にシフトするためである。

【0013】アルゴンの混入割合が5容量%よりも少ないと、プラズマが安定しただけのためスパッタすることが困難になる。一方、25容量%を超えると取り込まれるヘリウムの供給量が少なくなり、アルゴンのみでスパッタしたばかりと同様に応力制御性が悪いまとな

る。

【0014】

【発明の実施の形態】本発明のクロミウム薄膜の製造方法はスパッタターゲットにCrを用いる従来のように任意の通常のスパッタ装置にて実施することできる。